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Bearing Tests of Lubricant Additive Formulation and Pretreatment Processes

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13. ABSTRACT (*Maximum 200 words*)

It has been found that a new cleaning process, based on an aqueous alkaline detergent and implemented to eliminate the use of ozone-depleting chemicals from ball bearing processing, removes the protective layer formed on the bearing surface by a widely used anti-wear additive (tricresyl phosphate, or TCP) pretreatment. Accelerated laboratory bearing tests have been performed to investigate the effects on bearing wear life and performance of the additive pretreatment versus using oil formulated with the additive. These issues are of particular importance because bearings for several spacecraft mechanisms are currently cleaned with the new process; the bearing tests were conducted with a lubricant used in numerous momentum transfer wheels, Coray 100. The results of the wear tests and the post-test analyses have demonstrated that maximum benefit of TCP is obtained when the additive is formulated with the lubricant. Wear lives of the test bearings lubricated with formulated oil were found to improve by a factor of 15 over those lubricated with the base oil. Pretreated bearings had only a slight improvement in wear life (1.5X) when compared to untreated bearings in tests with unformulated oil. Profilometry performed on the flat counterfaces after testing revealed significant wear on bearings that operated without formulated oil and little wear on bearings tested with formulated oil. Based on these test results, little or no harmful effect is expected to arise from the use of the aqueous alkaline detergent cleaning method, provided that the bearings are lubricated with an oil containing an anti-wear additive.

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1. Introduction

The performance of liquid-lubricated spacecraft moving mechanical assemblies (MMAs) operating in the boundary lubrication regime depends strongly on the friction- and wear-reducing additives used with the oil. These additives function through chemical bonding and/or reaction with the surfaces of the mechanical components to prevent high friction and wear phenomena that occur when opposing surfaces contact one another during motion. One area of recent concern is the surface chemical effects of novel cleaning methods that have been developed to replace ozone-depleting chemicals (ODCs) in bearing processing. In particular, cleaning with more aggressive agents can significantly change the surface chemistry of steels and potentially alter the performance of lubricants and additives.

For many years, Freon, or CFC-113, found widespread use in the manufacture, cleaning, and lubrication of steel mechanical components. In fact, Freon became the solvent that defined many standard processes used by bearing manufacturers. To comply with Air Force guidelines to eliminate ODCs from nonessential usage, bearing manufacturers have developed new cleaning processes using a variety of different cleaning agents. In general, bearing performance criteria for the qualification of new cleaning processes have not been established.

One process, developed by Miniature Precision Bearings (MPB) Corporation, uses an aqueous detergent washing and a proprietary drying procedure to clean bearings prior to their lubrication. The new cleaning procedure has become MPB's standard method, and is currently being used to clean bearings for many spacecraft MMAs, including the reaction wheel bearings for the GPS IIR satellites. This process has been effective in removing a variety of contaminants from bearing surfaces, producing surfaces at least as clean as Freon-cleaned materials. Although this process has been demonstrated to be a suitable replacement for Freon in terms of cleaning ability, there have been some concerns regarding its use in conjunction with a commonly employed anti-wear pretreatment process for spacecraft bearings. In many applications, the metallic components of spacecraft bearings are treated with tricresyl phosphate (TCP) before lubrication. This compound forms a thin, phosphate-containing layer on the steel component surfaces that serves to lower both friction and metallic wear in bearings that operate under conditions of boundary lubrication. Typically, bearing components are treated with TCP at 110°C prior to lubrication, ostensibly to establish a protective coating, and TCP is usually formulated in the oil as an additive. Following the pretreatment process, the bearings must undergo a final cleaning prior to lubrication. This cleaning has been performed with Freon historically, but is now done with the detergent process at MPB. This has created concern because a previous study showed that the detergent cleaning method removes most, if not all, of the phosphate layer deposited during the pretreatment process.[1] In addition, the thickness of the oxide layer on the steel components is reduced after the detergent cleaning process. It is unknown whether the thinning of the oxide layer is a serious problem, but the removal of the phosphate layer is significant because the function of the additive may be drastically altered.

In order to determine the importance of the bearing pretreatment with TCP, a series of bearing performance and life tests were conducted with the Lubricant Screening Test Fixture. Testing was

conducted under four different lubrication conditions in order to simulate the effects of both the old and new cleaning procedures. The goals of these tests were to determine the merit of TCP pretreatment of bearing components and to determine if the omission of the pretreatment step in bearing processing causes any performance problems during subsequent operation. In particular, it was desired to determine if TCP formulation with the lubricating oil provided sufficient protection against metallic wear without any pretreatment. Following the wear tests, analyses were conducted on both the lubricant residuals and the bearing components in order to determine the extent of wear and lubricant degradation in the bearings.

2. Experimental

2.1 Testing

These bearing tests were conducted to determine the relative importance of TCP pretreatments versus TCP formulation in the lubricant. The tests also model some of the effects of the bearing cleaning processes. This was accomplished by running some tests with pretreated components (simulating a Freon cleaning) and other tests with non-pretreated components (simulating the worst-case aqueous alkaline detergent cleaning). The potential changes in bearing performance arising from other surface chemical effects of the detergent washing (thinner oxide, potentially non-wetting residue) are not addressed in this study. In addition, both unformulated Coray 100 and Coray 100 with 1% TCP were used in the testing. After the tests were completed, several different analytical techniques were used to evaluate the relative performance of each surface/lubricant condition.

The bearings used for the study were modified INA thrust bearings. The top raceway was a standard GT-1 thrust bearing, and the bottom raceway was a custom-made wear disk. Both the disk and the balls were made of the same material (52100 steel) as the bearings used in many spacecraft MMAs. The wear disks were polished flat to within 0.0002 in. and had a 2–4 microinch surface finish. The bearings had a 12-ball complement and utilized 0.188-in.-diameter balls. Stamped-steel retainers were used in these bearings.

The bearing wear tests were performed with the Lubricant Screening Test Fixture (Figure 1). This fixture, described in a previous report,[2] is designed to test lubricants to the point of failure under accelerated operating conditions. The severe test conditions in this apparatus result in relatively short test durations, thus allowing many tests to be performed. The main application of this testing approach has been the qualitative performance ranking of different lubricants.[2] In this work, the fixture is used to study the effects of lubricant additives on bearing performance. During the tests, the stationary raceway is intentionally misaligned with the rotating disk. This arrangement produces a large amount of sliding in the motion of the balls, and serves to accelerate the wear lives of the test bearings and lubricants by forcing the bearings to operate in a boundary lubrication environment. The misalignment also produces a relatively wide wear scar on the disk, facilitating post-test analysis.

Prior to the tests, the bearing components were cleaned ultrasonically in heptane and stored in a dry nitrogen environment. The bearings intended to be tested in the pretreated state were then subjected to a process similar to that used by the bearing manufacturer. This process consisted of submerging the bearing components in a beaker containing TCP and heating the mixture to approximately 110°C for 48 hours. After the completion of this step, the bearings were removed from the TCP, ultrasonically cleaned in heptane, and then stored in dry nitrogen. Prior to installation into the test fixture, the bearings were lubricated with 60 μL of lubricant. Depending on the condition to be tested, the oil used was either unformulated Coray 100 or Coray 100 formulated with 1% TCP. Table 1 lists the different surface/oil conditions used in the tests.

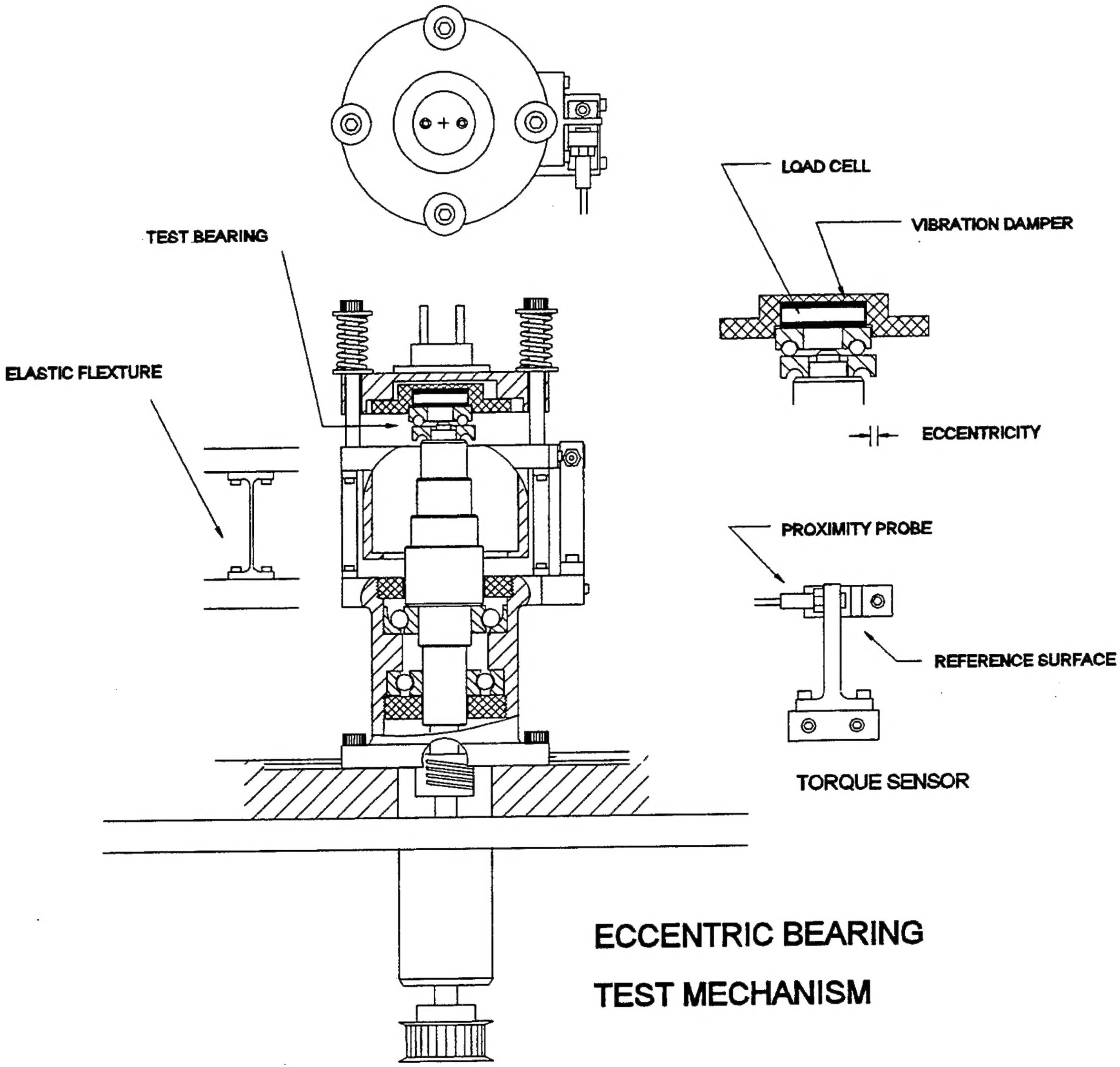


Figure 1. Test fixture assembly.

Table 1. Eccentric Bearing Test Conditions

Test Condition	No Pretreat	Pretreat	Unformulated Coray	Formulated Coray 100
1	X		X	
2		X	X	
3	X			X
4		X		X

The bearing tests were conducted under vacuum, at a pressure of approximately 1×10^{-7} Torr, and at temperatures that were slightly greater than the ambient (31–35°C). A water-cooled heatsink, mounted in indirect contact with the stationary raceway, was used to maintain the relatively low operating temperature (see Figure 1). The temperature is measured on the top bearing race and does not accurately measure the high temperatures that are generated in the contacts. In tests run without the heat sink, temperatures as high as 80–90°C are measured. The placement of the thermocouples provides "bulk" temperatures that can likely be more readily compared to measurements obtained from spacecraft hardware. The bearings were tested at a constant speed of 1400 RPM and an applied load of 60 lb (5 lb/ball). The load produced a peak contact stress of 300 ksi on the surface of the wear disk. This stress level is considerably higher than the maximum stress in many applications, but it was used as an acceleration factor to hasten the onset of failure.

During the tests, the reaction torque of the test bearings was monitored on a continuous basis. A custom computer program was used to record the torque data and to control the test fixture. The program accumulated high-speed torque data (100 Hz) and generated data files that were composed of time-averaged torque values. This method was employed to maintain continuous monitoring without storing an excessive amount of data. High-speed torque data were stored in data files on a periodic basis. These files represented 10-s "snap-shots" of the actual bearing reaction torque. In addition to the bearing reaction torque, the temperature of the test bearing was recorded from the pair of thermocouples mounted on the top race.

The bearing reaction torque was used as the criterion for determining when a test bearing had failed. Failure was defined as the point when the mean running torque exceeded the initial starting torque by a factor of three. Although the definition of failure was somewhat arbitrary, results from previous tests have indicated that both the contacting surfaces and the lubricant are significantly degraded by the time this torque level is reached. When the mean reaction torque exceeded this value, the computer program disabled the drive motor of the test fixture and stored the final data file.

2.2 Analyses

Several different post-test analyses were conducted on the bearing components and the lubricant residuals to determine the causes of failure and to provide a better understanding of the performance of the additive and pretreatment process. The analyses consisted of surface profilometry and Scanning Auger Microscopy (SAM) of the flat disk, and Supercritical Fluid Chromatography (SFC) on the residual oil.

The surface profilometry measurements were performed with a Rank Taylor Hobson Tally-Surf S5 surface profilometer. This instrument uses laser interferometry to measure the vertical displacement of a diamond-tipped stylus that moves across the surface of a specimen. The measurements from this instrument gave detailed information about the surface roughness of the wear disks and an estimate of the amount of wear that occurred in the wear-track during the testing.

The Auger analyses were performed with a Perkin Elmer PHI 590 spectrometer. This instrument was used to analyze both worn and unworn surfaces of at least one bearing disk for each test

condition. The data obtained from the spectra revealed the elemental composition of the bearing surfaces after testing and provided estimates of the extent of additive film formation on the contacting surfaces. During the analysis, Ar^+ ion sputter profiling was used to estimate the thickness of TCP-altered surface layers formed by either pretreatment or formulation.

The lubricant residuals were analyzed with a Dionex Series 600 supercritical fluid chromatograph. This instrument separates liquid samples into components based on the solubility of those components in supercritical CO_2. For a mixture of compounds in the same chemical family, e.g., alkanes, the components are separated approximately as a function of molecular weight. Both virgin oil and residual oil samples from the wear tests were analyzed with this device. The amounts of oil degradation and evaporative loss were determined by comparing chromatograms of the used and unused oils. In addition to this, the SFC was also useful for determining the relative amounts of TCP in the oil samples.

3. Results

3.1 Wear Life and Friction

A summary of the wear life results for all of the test conditions appears in Figure 2. Although there is a large amount of scatter in the results (probably due to the low quality of the test bearings), there are substantial differences in the wear lives of bearings tested under the various conditions. In Figure 2, the Table 1 test conditions progress from Condition 1 at the front of the graph to Condition 4 at the rear, with each bar representing a test to failure. The most striking difference is between the wear lives of the test bearings that were run with TCP in the oil (Conditions 3 and 4) and those that operated without formulated oil (Conditions 1 and 2). On average, TCP formulation in the oil increased the wear life of a test bearing by a factor of approximately 15 over tests with unformulated oil.

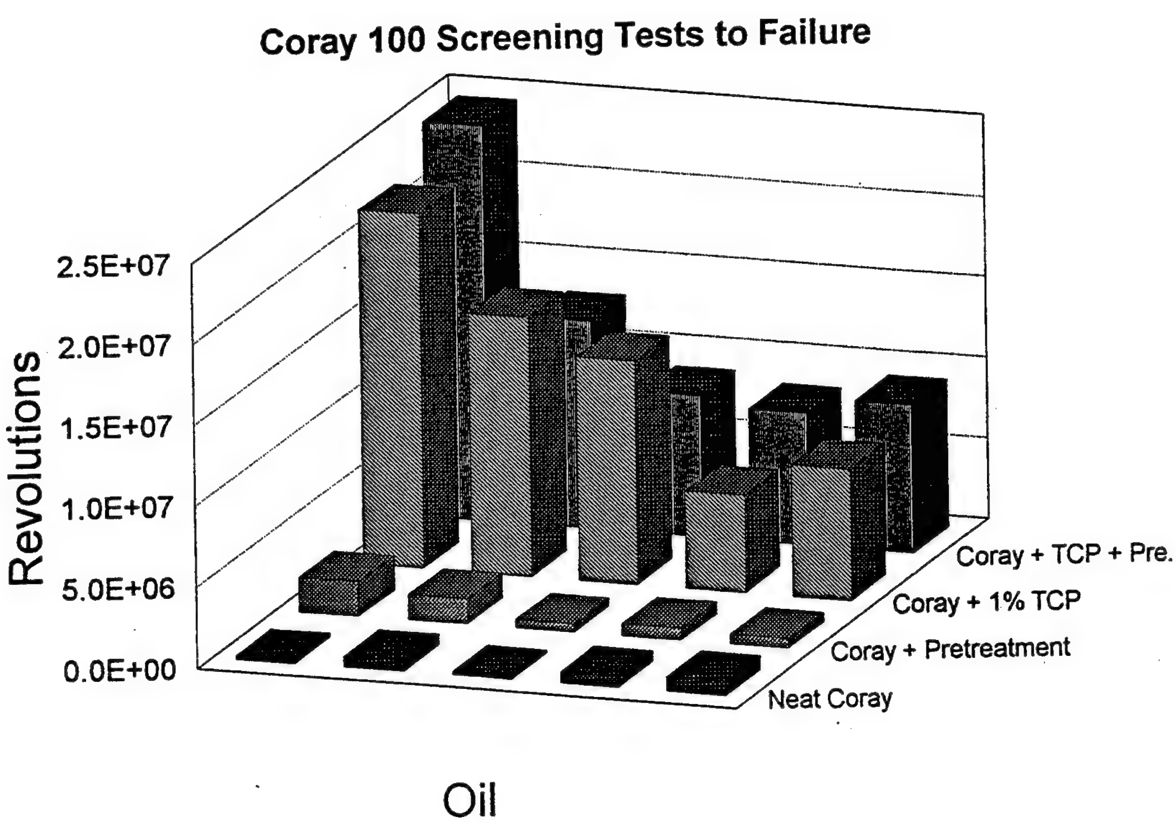


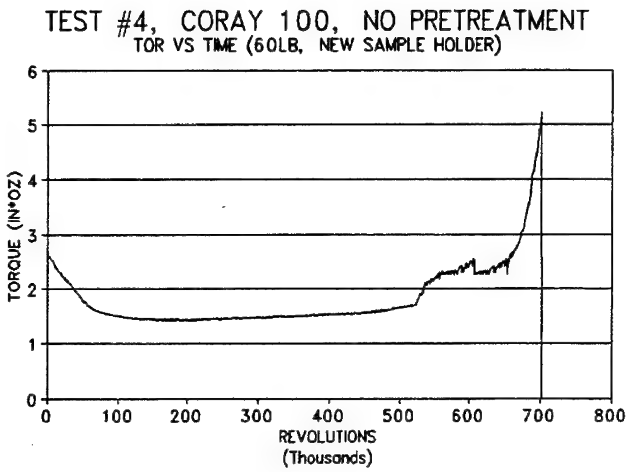
Figure 2. Summary of bearing test lives.

While test lives improved dramatically when formulated oil was used, little or no improvement was observed as a result of the pretreatment process. The tests conducted with neat (unformulated) oil and pretreated bearing components (Condition 2) exhibited, on average, a 1.5× improvement in wear life over tests conducted with the same oil and non-pretreated components (Condition 1). The tests performed with pretreated components and formulated oil (Condition 4) displayed essentially no improvement relative to tests with formulated oil without bearing pretreatment (Condition 3). From Figure 2, it is apparent that the maximum benefit of TCP in extending the life of a lubricated system occurred when it was used in formulation with the base oil.

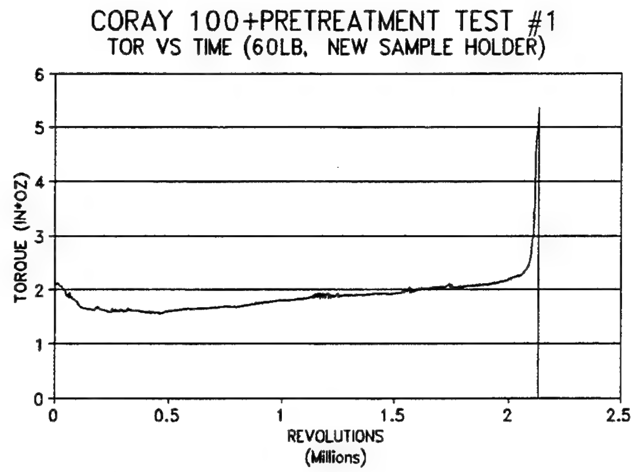
The reaction torque of the bearings was recorded during the tests, and representative results for each lubrication condition are presented in Figure 3. Each torque trace displays a run-in period of decreasing torque followed by a long period of relatively stable torque preceding a gradual rise in friction and rather sudden, catastrophic failure. The most important result from Figure 3 is that bearings tested with formulated oil tended to operate with lower steady-state torque than those with unformulated oil. On average, bearings tested with formulated oil operated with a mean torque level in the range of 0.8–1.5 in*oz, while bearings tested with unformulated oil had mean torque levels that ranged from 1.0–2.2 in*oz. There was no discernible reduction in the steady-state friction (torque) levels as a result of the pretreatment process. In Figure 3, it appears that pretreated bearings may have a lower initial torque level, which is evident in comparing the torque trace from Condition 1 to Condition 2, and Condition 3 to Condition 4. However, this trend was not observed in all tests, and the average initial torque value for all of the pretreated component tests was indistinguishable from those for the non-pretreated component tests. Further testing with greater attention paid to the effects of the additive on the bearing start-up torque would be beneficial since it is reasonable that pretreatment may provide a benefit early in bearing life.

3.2 Post–Test Analyses

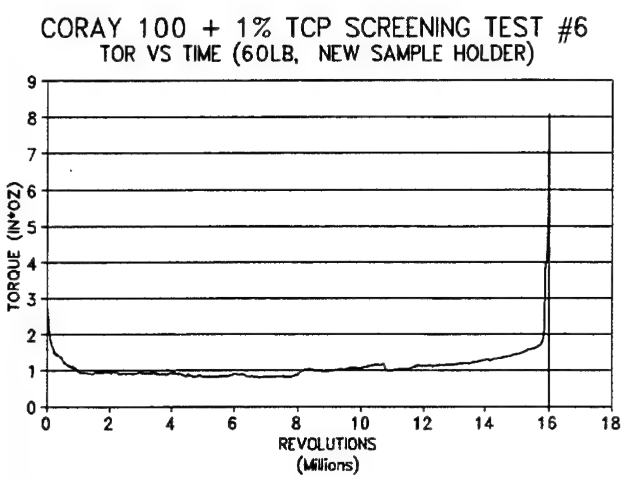
Figure 4 presents a representative sample of the post-test surface profile measurements made with the Taly-Surf instrument. The data in these graphs represent measurements of the surface topography of the flat specimens used in this work, showing both the surface roughness and the well-defined wear track from the test. The traces in Figure 4 are offset from one another to enable a comparison, making the y-axis divisions of 0.5 μm useful for comparing the wear scars and roughness values. In Figure 4, the trace from a Condition 1 test is presented at the top of the figure, and the traces progress down to a Condition 4 result at the bottom. The contact zone for each test is in approximately the same location on the chart, and is apparent as either an increase in surface roughness or a well-defined groove, or both. The surface profile of the flat from test Condition 2 (Test 13) revealed a significant wear scar (approximately 0.2 to 0.3 μm deep) and increased surface roughness in the contact zone. A similar finding, though not as severe, was observed in the case of test Condition 1 (Test 4). As indicated on the figure, Test 13 lasted approximately three times longer than Test 4 (a deeper track may be the result of greater endurance), and the untreated flat has very deep grooves (> 0.5 μm) at the edges of the wear track. In contrast to these results, the bearings that operated with formulated oil did not have distinct grooves in the contact regions. Even though the bearing from test Condition 3 (Test 7) operated 10 times longer than Test 13 and over 30 times longer than Test 4, this bearing exhibited only increased roughness in the contact region. The bearing race from test Condition 4 (Test



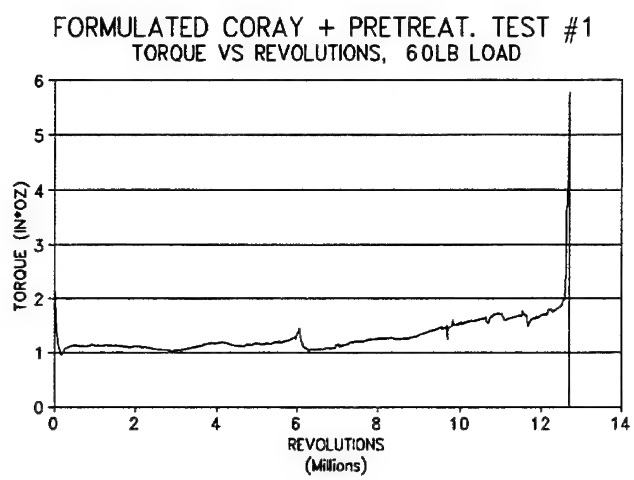
Condition #1



Condition #2



Condition #3



Condition #4

Figure 3. Representative torque traces of test conditions 1–4.

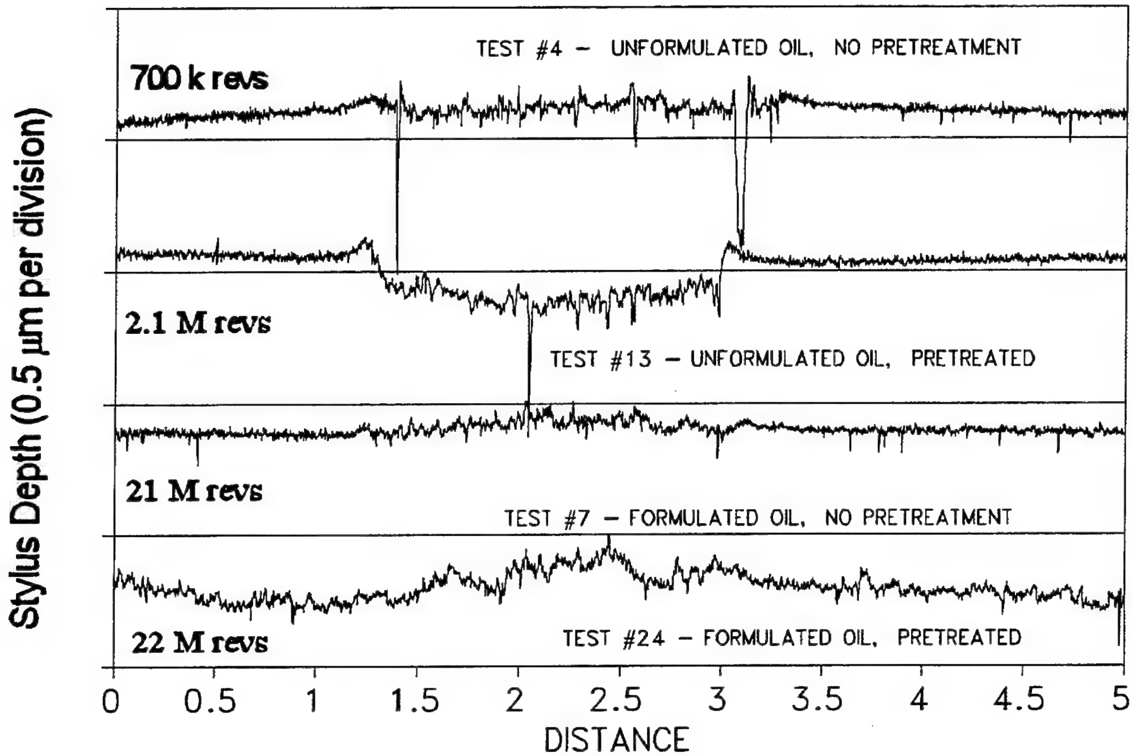


Figure 4. Surface profile scans across wear track on test flats. Additive study wear disk profiles 5-mm scans across wear tracks.

24) also showed very little wear, but did not demonstrate any noticeable improvement over that from Test 7. Each of the tests run with formulated oil may have even shown a slight build-up of material in addition to the surface roughening in the contact region. These profiles clearly demonstrate the wear prevention capability of TCP when it is formulated in the oil, and also confirm that the pretreatment of the bearing components provides little wear protection in long-term tests.

The results of the Auger analyses provide chemical insight into the performance of TCP pretreated parts and formulated lubricants. Although the exact mechanism by which TCP lubricates contacting surfaces is not fully understood, the presence of a phosphorus peak in the Auger spectrum from the bearing surface indicates that a phosphorus-containing film (formed by the adsorption and/or decomposition of TCP) has developed on the steel substrate. If Ar^+ ion sputtering is performed during this analysis to remove material, then it is possible to estimate the thickness of the additive film on the surface. Figures 5–7 contain spectra from the wear disks of two tests, one run under Condition 2 and one run under Condition 3.

In Figure 5, Auger spectra from an unworn region of a TCP-pretreated disk from a Condition 2 test are presented. The lower spectrum was obtained after a brief, 10-s sputter to remove surface contaminants and should be quite representative of the surface composition resulting from the

pretreatment. The spectrum shows a strong phosphorus signal near 120 eV, along with a weak carbon signal near 270 eV, a strong oxygen signal at 520 eV, and the characteristic three iron peaks ranging from 600 to 700 eV. After an additional minute of sputtering, the P signal has virtually disappeared and the O signal has dramatically decreased. Simultaneously, the Fe peaks are much stronger, as is the C signal, which has also acquired a peak shape that is characteristic of metal carbides. In short, after 70 s of sputtering, the surface layer that was altered by the TCP pretreatment has been removed by the sputtering process. With the calibrated sputter rate of 10 nm/min, this places an upper limit of the thickness of the surface layer altered by a standard pre-treatment at approximately 10 nm.

For comparison to Figure 5, the Auger spectrum from an area of the wear track of the same Condition 2 test is presented in Figure 6. This spectrum, acquired after a 10-s sputter, has a much smaller P signal than was observed on the unworn region after a similar sputter time. There is also a much stronger C signal that could be indicative of lubricant degradation in the contact, but the iron peaks are still visible, so this layer of material is either relatively thin or inhomogeneous. The key finding in the comparison of Figures 5 and 6 is the much smaller P signal in the wear track following the test, showing that the TCP-affected region is worn away during the test.

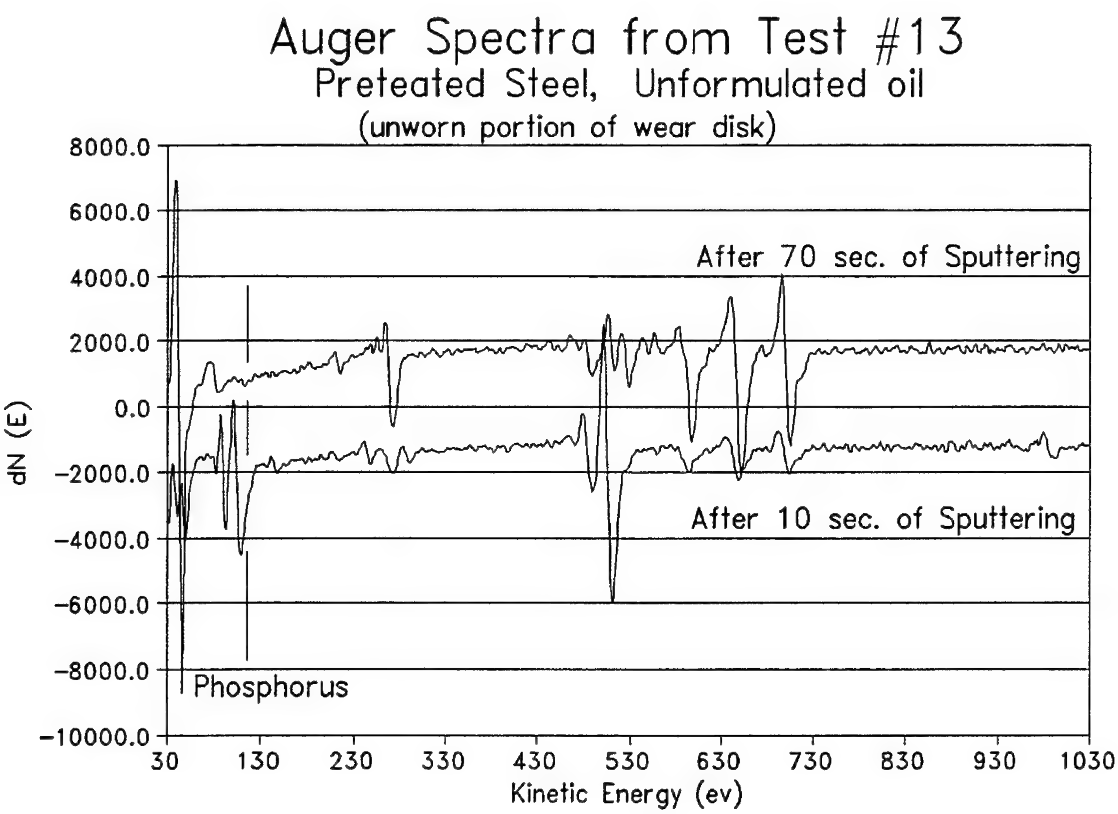


Figure 5. Auger spectra of condition 2 test flat, unworn region.

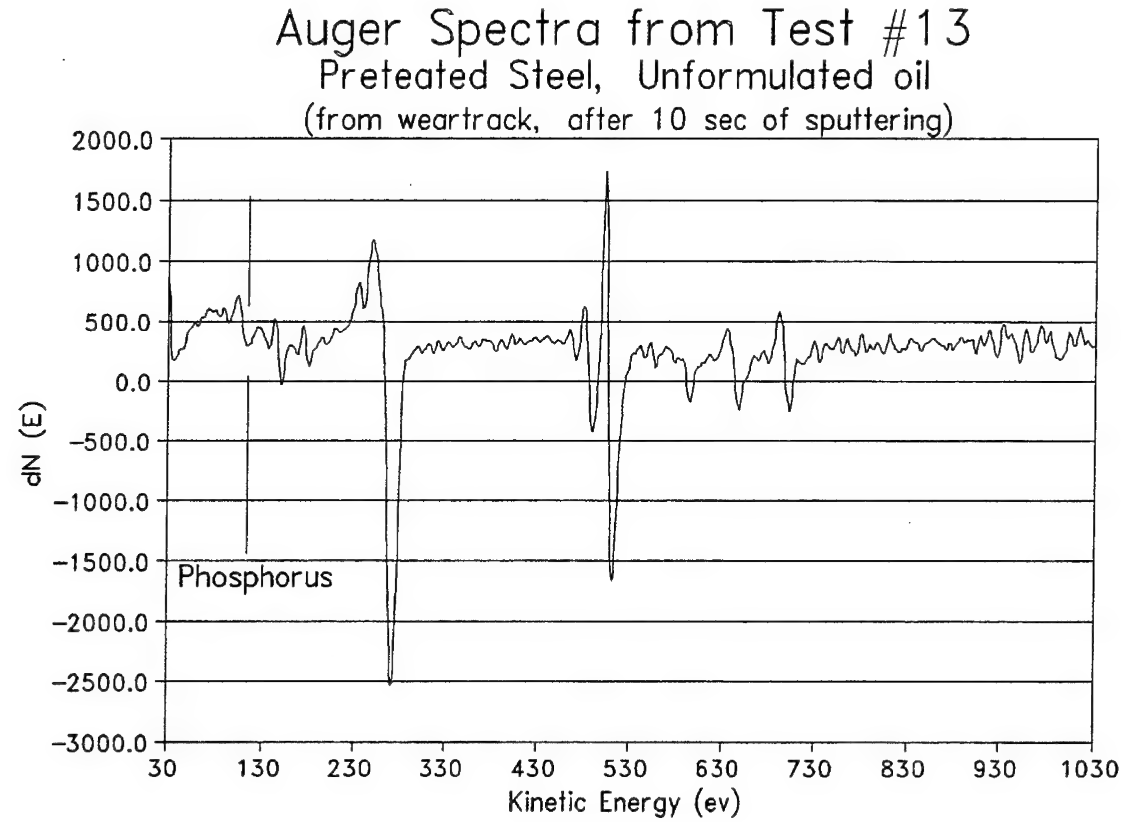


Figure 6. Auger spectrum of condition 2 test flat, worn region.

Figure 7 displays Auger spectra from the wear track of the flat from a Condition 3 test, where formulated oil was used, but the parts were not pretreated. After 40 s of ion sputtering, a very strong C signal is apparent along with weak P, O, and Fe features. It should be noted that relative to the iron signal, the phosphorus peak is quite strong, indicating that the P:Fe ratio is of the same order of magnitude as (although perhaps a factor of 2 less than) from the pretreatment. The Auger spectrum from the same spot is also provided after 600 s of sputtering, when approximately 100 nm (0.1 μm) of material have been removed from the surface. In this spectrum, the P signal is still evident, indicating that the TCP-affected layer extends much deeper into the surface when the bearing is run with TCP-formulated oil than is possible with the pretreatment. The increased roughness of the contact area (Figure 4) must be considered in such an analysis, potentially producing regions with thick C- and P-containing layers that may be shadowed and not effectively removed by the ion etching process. However, it is also possible that the increased roughness and apparent film build-up in the contact region revealed by the profilometry data indicate a layer of TCP-altered steel, on the order of 0.1–0.2 μm thick. Therefore, the result of running the test with the formulated oil may be that this chemically altered surface region is more resistant to wear than either untreated or TCP-pretreated steel.

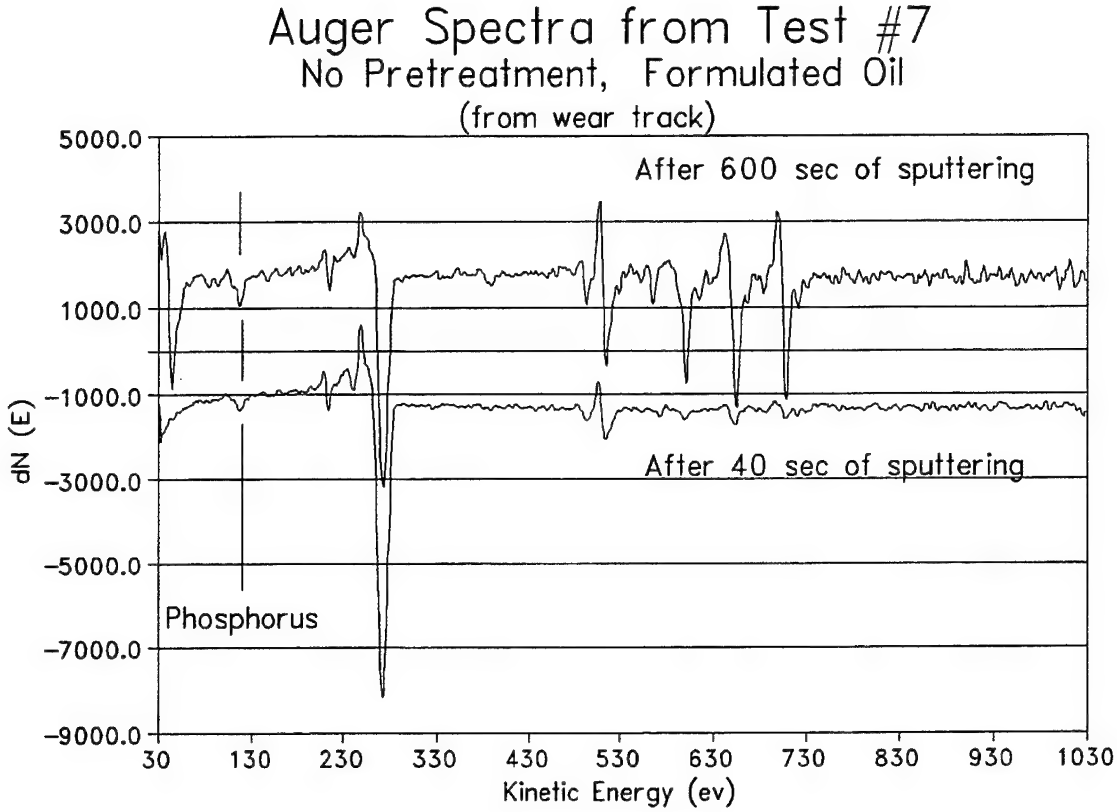


Figure 7. Auger spectra from the contact region of a condition 3 test flat.

The chemical changes occurring to the lubricant during the testing were examined using SFC. The SFC analyses of the formulated and unformulated virgin oil samples are presented in Figure 8. In examining these data, it is important to note the column retention times for the oil samples and the shape of the distribution of the various molecular species eluting from the SFC column. The absolute intensity of the chromatograph features depends on the sample size, which varied for the samples analyzed. Like other mineral oils, Coray 100 is composed of many different molecular weight components. In the SFC chromatograph, this type of oil will produce a broad band of peaks, as shown in Figure 8. The overall peak shape of the two unused oil samples is quite similar, with a broad, plateaued feature extending from approximately 10 min to 20 min retention time on the column. One significant difference between the two traces is the series of sharp peaks eluting from the column at approximately 13.5 min in the formulated oil. The sharpness of these peaks, their presence in the formulated oil, and SFC data of the neat additive (not shown) prove that these features are the various isomers present in the TCP additive. The presence of the TCP peaks in the same range of retention times as the virgin oil will provide some interesting information in the data obtained from the used oil samples.

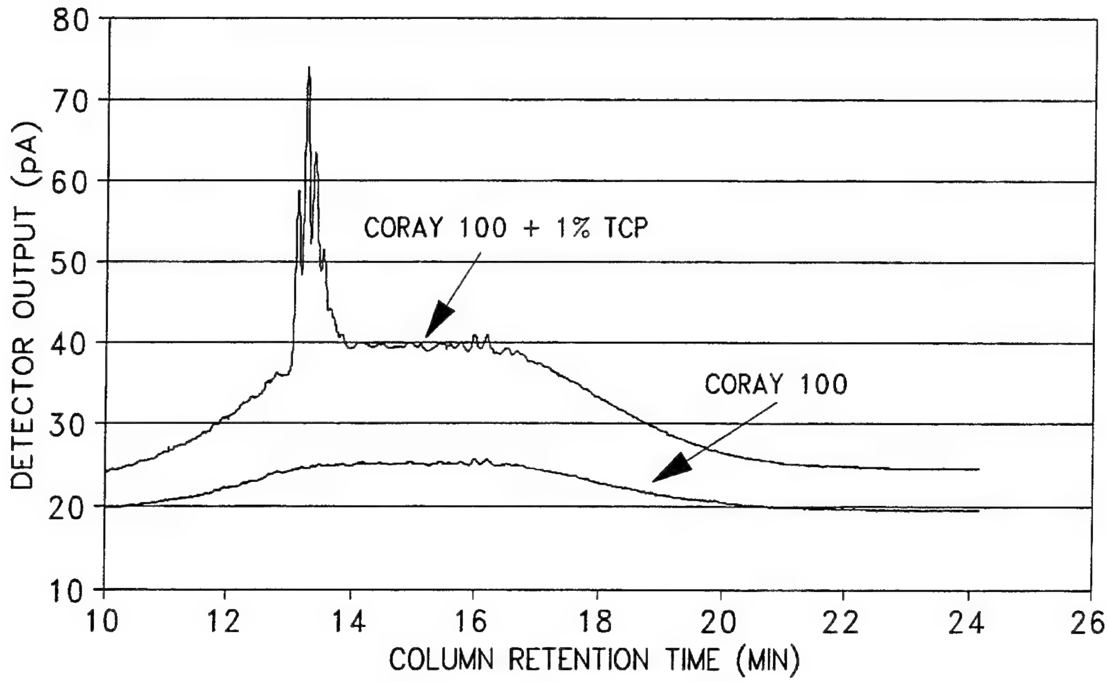


Figure 8. SFC analyses of unused oils.

Representative SFC data of the residual oil samples from the four different test conditions are provided in Figure 9. Comparisons between the chromatograms in Figures 8 and 9 reveal significant differences in the molecular weight distributions between the unused oil and the residuals from the longer tests (Conditions 2–4 with test durations $> 2 \times 10^6$ revolutions). The chromatograms of the test oil residuals clearly show a reduction in the relative intensity of the components with shorter column retention times. This change reflects the evaporation of the lower molecular weight, more volatile components from the oil. The oil from the Condition 1 test looks very similar to the unformulated virgin oil, while the other samples displayed extensive evaporation, losing most of the species that had retention times shorter than 14 min. The tests with the formulated oil showed the greatest amounts of evaporative loss due to their very long test times under vacuum. This result is of interest because the TCP peaks fall in this range of species lost due to evaporation, and it is readily apparent that the additive-related features are much weaker in the oil residuals than in the virgin formulated oil. It must be noted that the SFC data cannot be directly related to the relative volatility of the chemically different materials (TCP versus hydrocarbons), thus the loss of TCP could be due to evaporation, surface reaction, or both.

The SFC results for the formulated oil test samples (Conditions 3 and 4) in Figure 9 show additive peaks near 13.5 min that are very weak. This is particularly true of the Condition 3 oil sample (the trace with the weakest signal on the chart), where the additive peaks are virtually gone. This oil sample also had the greatest amount of evaporative loss from the basestock, so the smaller TCP features are likely due to the long test endurance and extensive time under vacuum. The SFC from Condition 4 had a small set of peaks corresponding to the

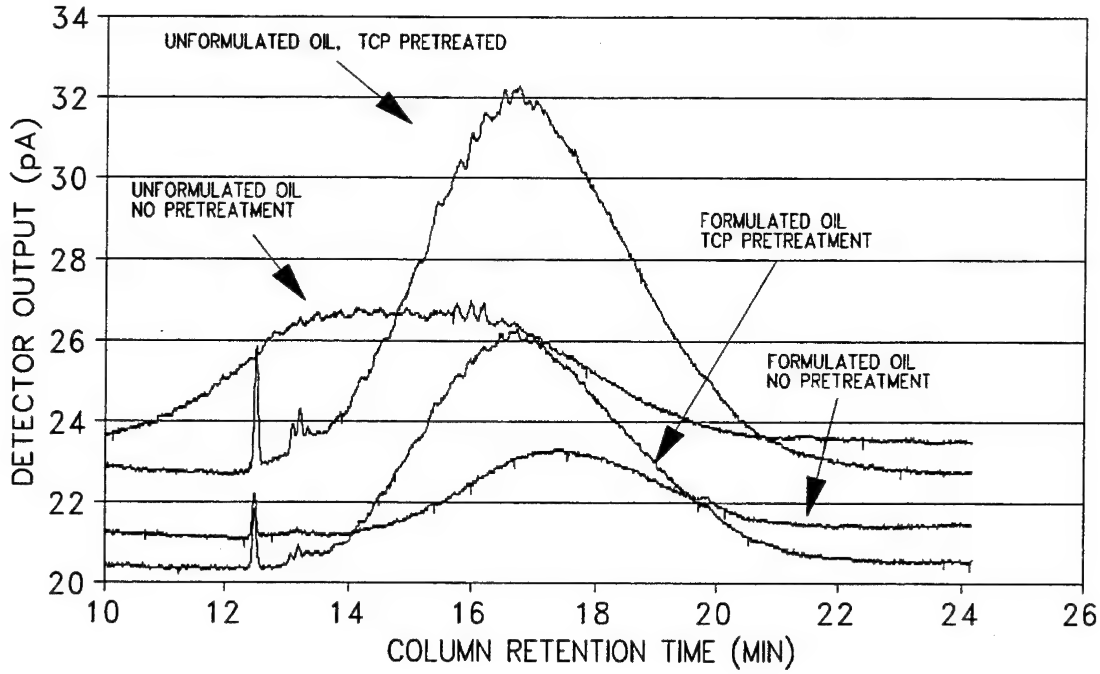


Figure 9. SFC analyses of oil residuals from eccentric bearing tests.

additive, and slightly less evaporative loss of the Coray. It is clear, therefore, that the residual formulated oil from the Condition 3 and 4 tests was almost completely depleted of TCP at the time of failure for the two tests presented, and this is likely a significant contributor to the eventual failure of tests with formulated oil.

In Figure 9, there are other interesting observations regarding the TCP that could provide some insight into the function of the additive. First, the SFC of the Condition 2 test residual oil definitely shows the presence of the TCP features. This is important because there was no TCP formulated with the oil for this test, but the parts were pretreated. This result provides clear evidence that the TCP residues from the pretreatment can be redissolved back into the oil, effectively removing some of the "protective" layer from the surface. Therefore, a significant amount of the TCP that bonds to the surface during pretreatment does so in a reversible, molecular fashion. This result also indicates that the pretreatment can supply some additive to the unformulated oil, which seems to be a more effective state for preventing wear, but the concentration of this in-situ formulation is inadequate for long life. Finally, all of the test samples that had either pretreated components or formulated oil display a peak near 12.5 min that isn't present in either formulated or unformulated Coray 100. This peak may be a decomposition product of the TCP interaction with the steel surface. Although we currently have not identified this feature, it may be important in determining the elusive tribochemical mechanism by which TCP protects steel surfaces.

4. Discussion

The results of the bearing tests and post-test analyses indicate that there are differences between TCP-based films formed by pretreating bearing parts and those created by operating a bearing with a TCP-containing oil. In general, the films formed during operation with TCP in the lubricating oil tend to be thicker and more durable than those formed by the standard pretreatment process. Consequently, bearing performance/life under boundary lubrication conditions is greatly enhanced when TCP is used as an additive in the lubricant instead of as a pretreatment only. The presence of TCP in the oil formulation provides a continuous source to replenish the surface layer. These tests may ultimately fail because the additive is lost through both surface reaction and evaporation. Another important result of this work is proof that TCP functions under vacuum. Although the presence of air facilitates the decomposition of TCP during pretreatment, neither oxygen nor water vapor is required for the additive to function in an operating bearing. While the testing and analysis performed for this report cannot fully explain the reasons for these results, the manner by which the boundary layer is formed may explain the findings.

During the bearing pretreatment process, the protective boundary-layer film is believed to form as a result of thermal decomposition and reaction of the TCP molecule with the steel surfaces.[3] Although the precise mechanism is not understood, TCP is known to have some reaction with iron (under an air atmosphere) at 110°C, and to react extensively at temperatures near 150°C.[4] Therefore, the treatment temperature is sufficient to initiate the surface reaction, but apparently results in only a thin surface layer of partially decomposed TCP. It is also important that the steel surfaces subjected to the pretreatment have an oxide layer, and it is this material, predominantly iron oxide, that interacts with the TCP bath. The film that remains on the steel surfaces after pretreatment and before cleaning is a combination of some partially reacted TCP and a significant amount of physisorbed, molecular TCP. Cleaning of these components with either heptane or Freon (both are relatively poor solvents for TCP) likely leaves some unreacted TCP on the surface, while more aggressive cleaning processes undoubtedly remove this material. The fact that some unreacted TCP was found in the oil after Condition 2 tests proves that a significant amount of molecularly adsorbed TCP remains after the pretreatment process and subsequent cleaning.

While bulk oil temperatures never approach the breakdown range of TCP during bearing operation, the localized heating that occurs in a contact zone can produce temperatures that are capable of fully decomposing TCP. When microscopic asperities come into contact in the wear zone, localized deformations of the metal can produce temperatures that are capable of melting the asperities. In addition, such contacts expose reactive metal species that are not present during the more benign pretreatment process. One final and important distinction between pretreatment and test conditions in this work is that the tests were run under vacuum while the pretreatment was performed in air, as is typical for space mechanisms. The different atmosphere can clearly lead to different surface chemistry of the additive, as has been observed for pretreatment under dry nitrogen relative to air.[4] All of these conditions likely cause localized decomposition of the TCP molecule and result in the formation of distinctly different surface reaction products in a working bearing than are formed during pretreatment. The profilometry results show that the film formed

by this tribochemical reaction in the presence of formulated oil provides excellent protection from wear.

Perhaps the most significant advantage of using formulated oil is its ability to resupply the contact region with an additive film during the course of operation. Test bearings lubricated with formulated oil were able to maintain their boundary protection for a much longer period of time than those lubricated with unformulated oil and, based on SFC oil analysis, seem to fail when the TCP is depleted from the oil (Figure 9). The similarity between the results from Conditions 3 and 4 indicates that the benefit of the pretreatment process, when combined with a formulated oil, is minimal at best and perhaps not essential for many applications. In fact, the risk of corrosion and damage to the bearing as a result of the pretreatment process may outweigh the benefit gained by this procedure.

It must be noted that eccentric bearing tests run under more stressful conditions with a synthetic hydrocarbon lubricant did show a life enhancement when both pretreatment and formulated oil were used.[5] The stressful conditions used in those tests (most significantly, higher temperature because no cooling was used) produced a much greater acceleration of the tests and may have altered the surface chemistry as well. However, the general finding of greater life extension with formulated oil relative to pretreatment alone was also observed in that work. An interesting result from that study was the demonstration that the protective film formed by operating the bearing with a formulated lubricant was much more effective than the film formed through pretreatment alone. In that particular test, a bearing was run with formulated oil for 180,000 revolutions and then cleaned and re-lubricated with unformulated oil. The test proceeded to run approximately three times longer than bearings operated with unformulated oil and normally pretreated components.

5. Conclusions

The results of the eccentric bearing tests and analyses in this report have shown that the TCP pretreatment process has a much smaller effect on bearing performance and wear prevention than operating with TCP-formulated oil. Under the stressful conditions used in this work, the pretreatment process provides a modest improvement in life. The film that does form during the pretreatment process appears to be a thin, partially decomposed layer of the additive along with some molecular TCP that does not prevent wear in long-term tests. This film is not very durable, with some material redissolving into the oil and with no significant means for replenishment once it has worn away.

TCP was found to be most effective when it was used as a formulated additive in the lubricant. The tests operated with formulated oil lasted much longer, ran with lower bearing torque, and showed much less wear at the conclusion of a test. The extreme pressures and localized heating that occur in the contact zone appear to enhance the decomposition of TCP and lead to the formation of a protective boundary-layer film. The presence of TCP in the oil ensures that the film can continuously rebuild as it is worn during operation. In fact, most tests of formulated oil may have failed only when the supply of TCP in the oil was exhausted through evaporation and surface reaction. Further testing under less stressful conditions should determine whether similar chemical interactions occur in angular contact bearings, and the collateral effects of the detergent cleaning process should also be addressed.

Based on these findings, no problems associated with additive performance are anticipated if the aqueous-alkaline detergent cleaning method is implemented (provided that a TCP-formulated oil is used). Furthermore, the data from the testing and analysis suggest that the pretreatment process might be omitted from the processing step without significant harm to the system, pending further testing of bearing performance under less stressful conditions. Since the scope of the study did not include the cleaning process directly, other factors, such as oxide-layer thickness and residual surface species, may require additional investigation.

References

1. S. V. Didziulis and R. Bauer, "Surface Analyses of Bearing Races Cleaned with Aqueous Alkaline Solutions," TOR–94(4470)–3, The Aerospace Corp., El Segundo, CA, 15 July 1994.

2. C. G. Kalogeras, M. R. Hilton, D. J. Carr, P. D. Fleischauer, S. V. Didziulis, "The Use of Screening Tests in Spacecraft Lubricant Evaluation," TR–93(3935)–6, The Aerospace Corp., El Segundo, CA, 15 October 1993.

3. E. S. Forbes, N. T. Upsdell and J. Battersby, *Inst. Mech. Engrs. Tribology Convention Papers*, C64172, 1973.

4. P. A. Bertrand, unpublished results.

5. S. V. Didziulis and R. Bauer, "The Volatility and Performance of Phosphate Ester Boundary Additives with a Synthetic Hydrocarbon Lubricant," TR-95(5935)-6, The Aerospace Corp., El Segundo, CA, 20 December 1995.

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